

Growth kinetics in ultrathin organic films

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INTRODUCTION

Thin films of large organic molecules are interesting model systems with respect to their technological importance. Nowadays, more and more applications of such materials are reported, e.g. in microelectronics, light-emitting devices, or photosensors. However, for many applications, the conventional films prepared by sublimation in high vacuum without control of the structural properties, are polycrystalline with lots of structural defects, which drastically influence the electronic and optical properties of such devices. Structural order becomes even more important in devices, where the formation of well-defined heterointerfaces of organic substances is preferred, e.g., when combining p- and n- conducting organic materials.

Previous experiments have demonstrated the influence of the metal-organic interface on the formation of different superstructures which extend into the third dimension and may lead to ideal epitaxial film growth. However, although polymorphic phases are known for many organic materials, it is difficult to optimize the growth conditions with respect to long-range ordered homogeneous films.

EXPERIMENT AND RESULTS

We have used XPEEM to investigate the film morphologies of ultrathin NTCDA films on Ag(111) for different growth conditions. NTCDA has been chosen since the molecular orientation in thin films can easily be manipulated by variation of the substrate temperature between 200 K and room temperature [1]. The experiments were performed at PEEM2 (BL 7.3.1.1). The Ag substrate was prepared by repeated sputter-annealing cycles. The NTCDA films were grown by vacuum sublimation in a separate preparation chamber. We recorded images for various photon energies to extract local NEXAFS/XANES spectra.

Fig. 1 shows XPEEM images two differently prepared films. The nominal film thickness varies by about 50 per cent for the two samples; the evaporation rate was estimated to about 1 monolayer per minute. Two different growth modes were detected: at elevated temperatures of 320 K the prominent structures are rectangularly shaped dark areas on a bright background. The high emission intensity is due to emission from the Ag substrate which is favored under these conditions for all photon energies, since the secondary electron yield (image formation in XPEEM without energy filter is primarily due to secondaries with low kinetic energy !) for Ag is much larger than for the organic compound. The dark areas are identified as NTCDA microcrystals. A closer inspection of their relative orientation yield angles of 60 and 120 degrees for their long axis. Thus, we may directly conclude that the underlying Ag(111) substrate, which has a 6-fold symmetry (with respect to its top layer) influences the growth direction.

Local NEXAFS spectroscopy clearly yields π^* -resonances characteristic for NTCDA monolayers in a chemisorbed surrounding [2] for areas in between the microcrystals. This indicates a Stranski-Krastanov growth mode, which is consistent with the relatively strong interaction between NTCDA and the metal substrate. LEED investigations reflect the diffraction

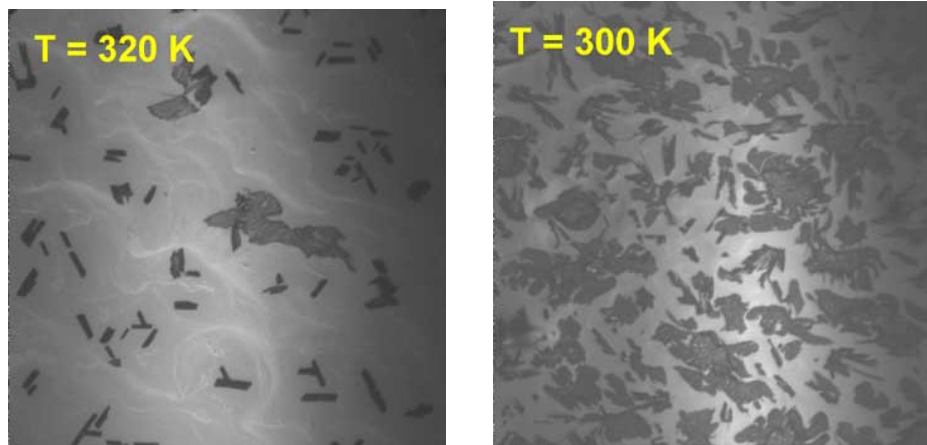


Fig. 1: NTCDA films (nominal thickness around 5 monolayers) adsorbed on Ag(111) at 320 K (left) and 300 K (right). Bright stripes correspond to bunched steps. Image size: $60 \times 60 \mu\text{m}^2$, $h\nu = 540 \text{ eV}$.

pattern of the monolayer species (for saturation coverage [3]) and support the finding from the NEXAFS spectra obtained from the bright areas.

For lower temperatures (300 K), the image looks very different. Instead of regularly shaped domains we find fractal growth of organic islands (Fig. 2, right). Compared to the film growth at elevated temperatures there is a much higher density of islands which is due to the smaller diffusion length. In addition, the individual islands are not homogenous. We attribute this finding to the mismatch of the structural parameters. So far, no experimental evidence is found for epitaxial growth of NTCDA/Ag(111). The LEED pattern in this case is diffuse and shows only broad diffraction spots consistent with the small domains. From other experiments (HREELS) there are indications that this film has a different molecular orientation compared to the high- and low-temperature phases, respectively [1].

From the present geometric setup at PEEM2 it is unfortunately not possible to derive the local molecular orientation from NEXAFS dichroism. Future experiments will focus on in-situ prepared films to investigate the growth kinetics during adsorption and thus allow the investigation of adsorption processes on a real-time scale. Proper image analysis may give direct access to diffusion parameters (diffusion length, activation energies). In this respect, XPEEM will offer new opportunities and thus overcome present limitation by scanning probe or laterally averaging spectroscopic techniques.

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This work was supported by the Bundesminister für Bildung und Forschung, contracts 05SL8WW18. We gratefully acknowledge experimental support by A. Scholl and A. Doran during the experiments at PEEM2.

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